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# PATENT SPECIFICATION

(11) 1 473 240

- (21) Application No. 27752/74 (22) Filed 21 June 1974  
 (31) Convention Application No. MA 2483 (32) Filed 21 June 1973 in (19)  
 (33) Hungary (HU)  
 (44) Complete Specification published 11 May 1977  
 (51) INT CL<sup>2</sup> G01N 27/62//31/08  
 (52) Index at acceptance  
 G1N 310 311 314 31X



## (54) CATALYTIC DOUBLE DETECTOR, PARTICULARLY FOR THE ANALYSIS OF SULPHUR- AND/OR NITROGEN-CONTAINING ORGANIC COMPOUNDS

(71) We, MAGYAR ASVANYOLAJ ES FOLDGAZ KISERLETI INTEZET, of 1, Wartha Vince u., Veszprem, Hungary, a Body Corporate organised under the laws of Hungary, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a catalytic double detector. The invention may be applied particularly to the analysis of sulphur and/or nitrogen-containing organic compounds.

In gas chromatography flame ionization detectors are extensively used (e.g. British Patent No. 1,127,173 and F. P. Speakman—K. W. Brittan, Flame ionization detectors, 92.1695) for analysis of hydrocarbons and hydrocarbon derivatives. In these detectors the hydrocarbons and hydrocarbon derivatives burn, while a charge proportional to the carbon content of the compound flows through the detector. In course of burning by consumption of air or O<sub>2</sub> the sulphur content is transformed to SO<sub>2</sub> and the nitrogen content to nitrogen oxides.

In gas chromatography electron capture detectors are likewise known (D. Jentzsch and E. Otte: Detektoren in der Gas-Chromatographie, 1970. Frankfurt/M., Akad. Verl. Ges.), based on the measurement of recombination ionic current diminution due to the electron capture property of some compounds. A special variant of electron capture detectors are aerosol detectors, in which electron capture by aerosol particles causes an affect which is detected.

The two kinds of detectors may be operated without any difficulty in parallel, but in series connection they interfere with each other.

For measuring halogen-, sulphur- and nitrogen containing compounds coulometric and electrochemical detectors respectively may be used (see the book mentioned above). Handling of these however, is very tiresome and sets up difficult requirements to the user. In gas chromatography difficulties arise due

to ensuring perfect combustion and due to the fact that the effective volume of these detectors is appreciable.

Double detectors too, are known in gas chromatography. For measuring halogens and phosphorus containing compounds, alkaline thermo-ionization detectors (see the book mentioned above) may be used, in which a platinum wire soaked with alkaline salts is placed in a flame and its thermal ionization increases in the presence of phosphorus or a halogen. In the case of photometric detectors (S. S. Brody and J. E. Chaney: Flame photometric detectors, Journal of Gas Chromatography, 4(1966), p. 42—46 and M. L. Selucky: Specific gas chromatography detectors, Chromatography, 4 (1971), p. 425—454), the light emission of sulphur and phosphorus compounds burning in a hydrogen flame is used for detecting these compounds. In these detectors instability of the basic current and sensitivity depending on different parameters causes a problem.

For the measurement of the concentration of sulphur-containing air pollution substances, a method and apparatus are likewise known (our Hungarian patent application basic No. MA—2358, dated 12 May 1972 now open to public inspection), being in the art of catalytical transformation and in measurement of SO<sub>2</sub> having electron captive properties, similar to those contained in the present application. Nevertheless it is not suited as a flame ionization detector for the indication of organic carbon compounds, since oxidation is not being carried out by oxygen, but by air consumption and the method is not suited for gas chromatographic applications.

The present invention provides a catalytic double detector for analysing organic compounds, comprising a flame ionization detector, a microreactor and an electron capture detector, the microreactor being downstream of and in communication with the flame ionization detector for receiving a gas stream containing combustion products from the flame ionization detector and for catalytic oxidation of constituents of the gas stream,

the electron capture detector being downstream of and in communication with the microreactor.

5 In the microreactor, the combustion products of the flame ionization detector, e.g.  $\text{SO}_2$  and/or nitrogen oxides are transformed by heterogeneous catalysis into products of high electron capture cross-section so that the  
10 electron capture detector generates a signal proportional to the sulphur and/or nitrogen content of the compounds being analysed.

The microreactor inserted between the two detectors, has a very important and versatile role.

15 1. It promotes the conversion of  $\text{SO}_2$  and nitrogen oxides into  $\text{SO}_3$  and  $\text{NO}_2$  ensuring high sensitivity of electron capture detection, thereby.

20 2. It assists complete oxidation of hydrocarbons; since products arising from incomplete combustion would generate signals in the electron capture detector.

25 3. By operation at different temperatures, the microreactor is able to optimise the production of either  $\text{SO}_3$  or  $\text{NO}_2$  and thereby to distinguish between sulphur and nitrogen compounds. For a given volume flow rate, the conversion  $\text{SO}_2$  to  $\text{SO}_3$  has a maximum efficiency at a particular reactor temperature.  
30 This maximum occurs because with increasing temperature the velocities of chemical reactions increase, whilst the equilibrium constant becomes less favourable to the production of  $\text{SO}_3$ . In the case of  $\text{NO}_2$ , the optimum  
35 temperature lies below that for  $\text{SO}_3$ . However, it is not possible to use such low reactor temperatures, because it is necessary to maintain the after-burning effect of the reactor. This conflict of requirements for maximising  $\text{SO}_3$  or  $\text{NO}_2$  production may be avoided by connecting reactor sections with higher and lower temperatures one after the other.

40 4. Due to the heating, condensation of water vapour and its disturbing effects on the electron capture detector are prevented.

45 For production of  $\text{SO}_3$  in addition to platinum other catalysts are also known. However, since platinum also catalyzes the formation of  $\text{NO}_2$ , platinum catalysts are of primary  
50 interest.

The roles performed by oxygen added to the mixture to be analysed are as follows:—

55 1. Operating the flame ionization detector.  
2. Preventing water vapour condensation.  
3. Enabling the microreactor to oxidize hydrocarbons.

4. Diminishing the dwell time of individual gas chromatographic components, and thereby allowing the effective volume of the electron  
60 capture detectors to be reduced.

5. Rendering more complete the conversion to  $\text{SO}_3$  and  $\text{NO}_2$ .

65 When considering the thermal conditions in the double detector, the following is worthy of mention. The temperature of the gas

chromatographic column hardly influences the operation of the double detector; a fact which is very advantageous from the point of view of practical application.

70 The mode of action and the operating voltage of the electron capture detector is important since the highly electron trapping substances (for example,  $\text{SO}_2$  or  $\text{NO}_2$ ) are present in only trace amounts in an excess of gas  
75 (i.e.  $\text{O}_2$ ) which also has electron trapping properties. In pulse mode operation (at low electron energy levels) high sensitivity to  $\text{SO}_2$  and  $\text{NO}_2$  cannot be expected; therefore the use of d.c. voltage which  
80 also has the advantage of enabling sulphur and nitrogen compounds to be discriminated, is preferred.

The present invention also provides a method of analysis for sulphur and/or nitrogen of mixtures including sulphur- and/or  
85 nitrogen-containing organic compounds, comprising burning the mixture with oxygen or air in a flame ionisation detector, passing the combustion products therefrom to a microreactor which is at a temperature in the range  
90 100 to 800°C and contains a heated platinum wire catalyst, passing the combustion products from the microreactor to an electron capture detector and detecting therein the  $\text{NO}_2$  and/or  $\text{SO}_3$  present in the combustion products. 95

The invention further provides a method of analysis for sulphur of mixtures including sulphur-containing organic compounds, which  
100 comprises burning the mixture with oxygen or air in a flame ionization detector, passing the combustion products therefrom to a microreactor which is at a temperature in the range 500 to 600°C and contains a heated platinum wire catalyst, passing the combustion  
105 products from the microreactor to an electron capture detector and detecting therein the  $\text{SO}_3$  present in the combustion products.

In addition the invention provides a method for analysis of nitrogen of mixtures including nitrogen-containing organic compounds, which comprises burning the mixture  
110 with oxygen or air in a flame ionisation detector, passing the combustion products therefrom to a microreactor which is at a temperature in the range 400 to 500°C and contains a heated platinum wire catalyst, passing the mixture to an electron capture detector and detecting therein the  $\text{NO}_2$  present  
115 in the combustion products.

In the course of our experiments it has  
120 been found that the temperature of the microreactor should be for reactors which have a single microreactor section, as follows:—

For maximising the sensitivity to sulphur containing compounds a temperature  
125 between 400 to 800°C, expediently 550°C.

For maximising the sensitivity to nitrogen containing compounds a temperature

between 100 to 600°C, expediently 400 to 450°C.

In the case of microreactors having two sections, for the first section the temperature is expediently 450°C, and the temperature is from 100 to 150°C for the second section.

The invention is further described below by way of example only with reference to the accompanying drawings, in which:—

Figure 1 shows a catalytic double detector according to the invention;

Figure 2 shows a block diagram of the apparatus used to make measurements;

Figure 3 shows chromatograms achieved by double detecting a sulphur-containing model mixture;

Figure 4 represents a chromatogram of a gasoline; and

Figures 5a and b show chromatograms of a thiophene and pyridine containing model mixture by using two different operating conditions of the double detector.

In Figures 3, 4, 5a and 5b the full line relates to the gas mixture signal obtained from the flame ionisation detector and the broken line relates to the signal from the electron capture detector.

The catalytic double detector shown in Figure 1 consists of three main parts: a flame ionization detector 1, a microreactor 2 and an electron capture detector 3. For practical purposes, to the commercially available flame ionization detector an extension comprising the parts 2 and 3 is tightly fitted. In this modification the extension does not affect in any respect the operation of the flame ionization detector.

The flame ionization detector 1 is connected by stud 4 to a gas chromatographic column and pipe 5 serves for the introduction of hydrogen, pipe 6 for oxygen. To terminal 7 a d.c. voltage is connected, and at the same time current from a collector electrode 8 is lead through a terminal 9 to an amplifier. The pipe end 10 (which serves for exhausting combustion products when the extension is not fitted) is closed, so that the oxygen and also the combustion products (together with the small amount of nitrogen serving as carrier gas) is forced to pass towards the microreactor 2.

The extension comprising parts 2 and 3 may be tightly fitted by an O-ring gasket made of silicon rubber to the flame ionization detector 1.

In the microreactor 2 a Teflon seal (Teflon is a Registered Trade Mark) carries a refractory glass tube 13, in which soldered-in platinum contacts 14 carry an electrically heated platinum wire 15. Teflon stoppers 16 and 17 allow for sealing and fixing the contacts into the microreactor.

Cooling ribs 18 of the extension effect cooling of gases leaving the microreactor 2.

In the electron capture detector 3 the ionization level is created by a  $\beta$  radiation source 19, while to an electrode 20 a d.c. voltage is connected to collect the ions formed onto the electrode. The current from the detector is lead through a Teflon insulator 21 via a cable 22 into an amplifier. Through the bore holes 23 gases are exhausted from the detector. A stopper 24 closes up and screens the connecting point of the measuring electrode 20 and the screened cable 22.

The following Examples illustrate the operation of the double detector described above.

#### Example 1

##### Analysis of sulphur-containing samples

The block diagram of the apparatus used for testing is shown in Figure 2. Gas chromatographic separation was carried out by a gas chromatograph 25 type Pye 104. The catalytic double detector 26 (the block 26 diagrammatically represents the apparatus shown in Figure 1) was connected to the exit point of the capillary column of the gas chromatograph 25.

The voltage to the flame ionization detector 1 was supplied by, and the ionization current was measured by, an ionization amplifier 27 of Pye. The heating current to the microreactor was supplied by a stabilized feeding unit 28. For operating the electron capture detector a feeding apparatus 29 was used. For measuring the variation of the ion current, an amplifier 30 type Carlo Erba SS 445 (Carlo Erba is a Registered Trade Mark) was used. The signals from the amplifiers 27 and 30 were recorded by a Kutesz multi-channel recorder 31.

The applied gas chromatographic conditions were as follows:

Conditions in the column 25:—

Column: 50 cm long, i.d. 0.25 mm acid resisting tube, wetted by OV-101 wetting agent.

Gas chromatograph conditions:—

Temperature: 140°C.

Flow velocities:

N <sub>2</sub>	50 ml/h
H <sub>2</sub>	1.2 l/h
O <sub>2</sub>	36 l/h

Sample: 2  $\mu$ l model mixture

Attenuation: 12:1

The microreactor was 42.5 cm long and 0.07 mm in diameter Pt (10% Rh). Temperature of the microreactor, as measured by a Fe-constantan thermocouple, was 545°C.

Specification of the electron capture detector:—

$\beta$  radiation source: 10 mCi Ni-63 isotope

Voltage: 5 V

Operating temperature: 95°C

Composition of the measured model mixture:—

- 0.1% by volume thiophene  
 0.1% by volume 2 - methyl - thiophene  
 0.1% by volume 3 - thia - heptane  
 0.1% by volume 3,5 - dimethyl - 4 - thia - heptane  
 0.1% by volume 3,4 - dithia - heptane dissolved in n - decane.
- Amplifier:—  
 flame ionization amplifier 27:  $1 \times 10^4$   
 (attenuation factor)  
 electron capture amplifier 30: 10/2  
 (attenuation factor)
- Recorder:—  
 measuring range: 2 mV  
 chart speed: 600 mm/h
- The obtained gas chromatographic trace and the sulphur chromatographic trace are shown in Figure 3. (For technical reasons the sulphur chromatogram has been shifted by 2 mm). Well to be observed is, that in the flame ionization detector the decane and sulphur compounds produce a signal, whilst in the electron capture detector only the sulphur compounds produce a signal.
- Under given circumstances sensitivity of the double detector to sulphur is: 103 coulomb/g S, which may be considered good.

#### Example 2

##### Analysis of a gasoline

- The apparatus used and the operating conditions were the same as in Example 1 except that:

- Temperature of the column 25: 120°C  
 Sample: 10  $\mu$ l gasoline from Um-el-Yasr originating crude oil of boiling range; 84—180°C  
 Flame ionization amplifier 27:  $20 \times 10^4$   
 (attenuation factor)

- The recordings obtained are shown in Figure 4.

#### Example 3

##### Analysis of a sulphur and nitrogen-containing model mixture

- The apparatus used and the operating conditions were as in Example 1 except that:

- Measurement: 1  $\mu$ l 10% by volume pyridine  
 1% by volume thiophene  
 89% by volume decane  
 Temperature of the column 25: 150°C  
 Temperature of the microreactor 2  
 experiment a) 545°C  
 experiment b) 435°C  
 Voltage of the electron capture detector  
 experiment a) +5V  
 experiment b) +4V

The obtained results are shown for case a)

in Figure 5a and for case b) in Figure 5b. By comparing the results of experiment a) with those of experiment b), the sensitivity in case b) to nitrogen increases by 2.9 times and that to sulphur is reduced by 57%. This allows, using chromatographic analysis made under two different conditions, e.g. experiments a) and b), the compounds containing sulphur and nitrogen to be discriminated.

The double detector may be used, in addition to the already described gas chromatographic measurements, for the determination of sulphur and/or nitrogen content of organic samples on an absolute basis. In this case the flame ionisation detector generates a signal proportional to the measured amount of matter (or more precisely to the carbon content), and the electron capture detector a signal proportional to the sulphur, and/or nitrogen content. When these signals are compared with signals obtained from known quantities of materials, an exact elementary analysis may be carried out from a very small amount of a sample. In this case no gas chromatographic separation is necessary, but when nevertheless effected, evaluation may be carried out by using automatic numerical integrators.

The catalytic double detector could be used in addition to sulphur and nitrogen determination also for detecting other elements present in organic compounds, in course of which an aerosol combustion product is formed, e.g. in combustion of volatile phosphorous compounds  $P_2O_5$  is formed, which has such an electron capture cross-section as to enable phosphorus to be detected with a similar sensitivity as sulphur. The situation is similar also in detection of organic compounds containing halogens, arsenic, antimony, silicon, lead. In these cases the microreactor enables the hydrocarbon traces to be completely combusted so as to allow the subsequent use of an electron capture detector.

#### WHAT WE CLAIM IS:—

1. A catalytic double detector for analysing organic compounds comprising a flame ionization detector, a microreactor and an electron capture detector, the microreactor being downstream of and in communication with the flame ionization detector for receiving a gas stream containing combustion products from the flame ionization detector and for catalytic oxidation of constituents of the gas stream, the electron capture detector being downstream of and in communication with the microreactor.

2. A detector as claimed in Claim 1, wherein the flame ionization detector has an inlet for hydrogen, an inlet for oxygen, a terminal for connection to a d.c. voltage source, a collector electrode and a terminal contacting the collector electrode, the microreactor has an electrically heated platinum wire and a cooler downstream of the platinum wire, and

the electron capture detector has a radiation source.

3. A detector as claimed in Claim 1 or Claim 2, wherein the microreactor comprises one or more sections, the temperature of each section being independently adjustable.

4. A method of analysis for sulphur and/or nitrogen of mixtures including sulphur- and/or nitrogen-containing organic compounds, which comprises burning the mixture with oxygen or air in a flame ionisation detector, passing the combustion products therefrom to a microreactor which is at a temperature in the range 100 to 800°C and contains a heated platinum wire catalyst, passing the combustion products from the micrometer to an electron capture detector and detecting therein the NO<sub>2</sub> and/or SO<sub>3</sub> present in the combustion products.

5. A method of analysis for sulphur of mixtures including sulphur-containing organic compounds, which comprises burning the mixture with oxygen or air in a flame ionization detector, passing the combustion products therefrom to a microreactor which is at a temperature in the range 500 to 600°C and contains a heated platinum wire catalyst, passing the combustion products from the micro-

reactor to an electron capture detector and detecting therein the SO<sub>3</sub> present in the combustion products.

6. A method of analysis for nitrogen of mixtures including nitrogen-containing organic compounds, which comprises burning the mixture with oxygen or air in a flame ionisation detector, passing the combustion products therefrom to a microreactor which is at a temperature in the range 400 to 500°C and contains a heated platinum wire catalyst, passing the mixture to an electron capture detector and detecting therein the NO<sub>2</sub> present in the combustion products.

7. A double catalytic detector substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

8. A method of analysis for sulphur and/or nitrogen from mixtures of sulphur and/or nitrogen containing organic compounds substantially as hereinbefore described in any one of Examples 1 to 3.

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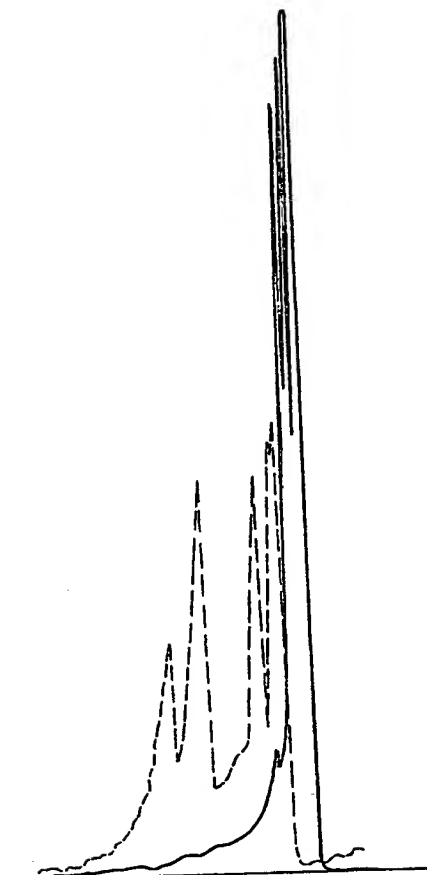
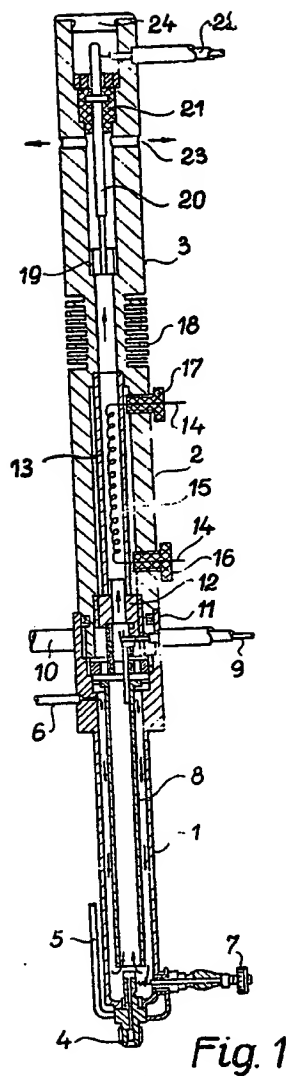
Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
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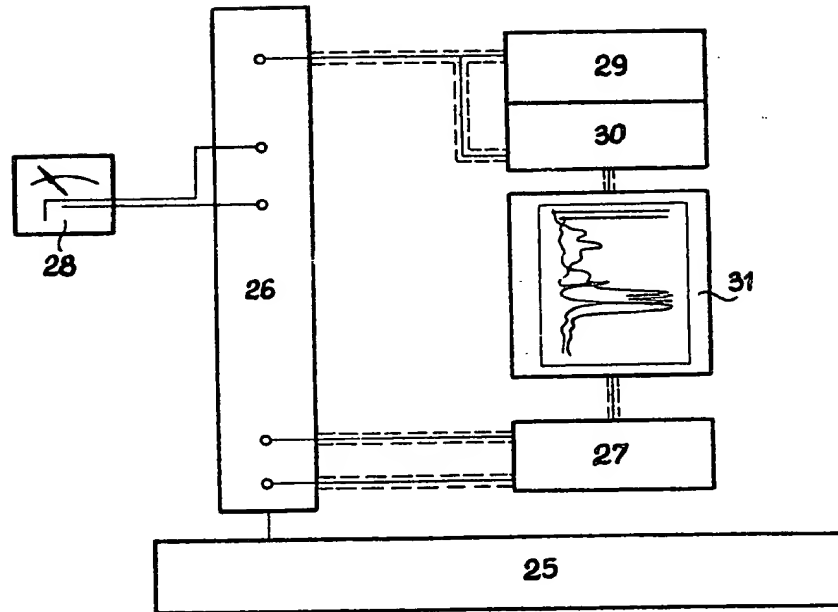
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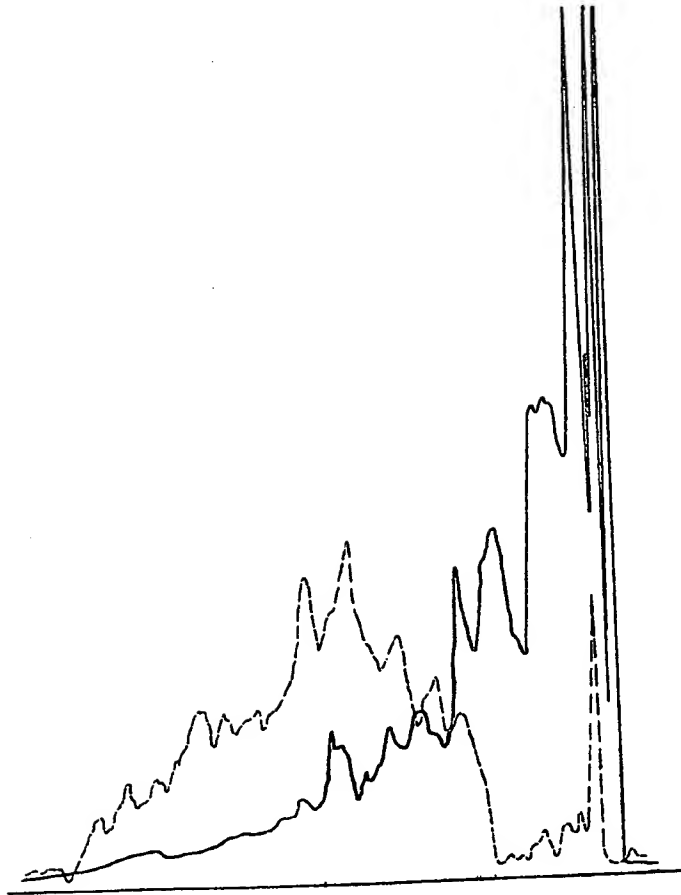
*Fig. 2*

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*Fig. 4*

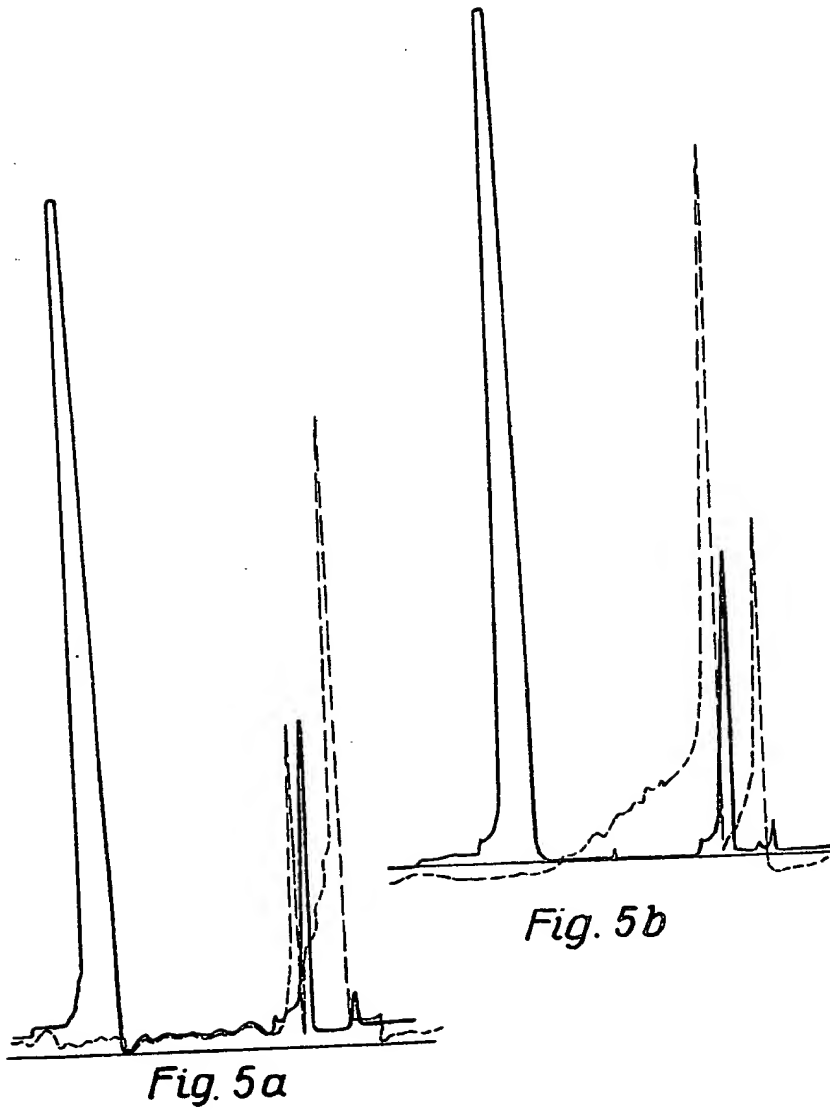


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